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**Relation between phosphate accumulation, soil P levels and
P leaching in agricultural land**

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ABSTRACT

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In order to evaluate the impact of manure application on soil P fertility and P leaching, a study was carried out to relate phosphate accumulation to soil P level and P leaching. Based on the behaviour of P kinetics, it is possible to derive a description for P availability. If the P availability is based on a water extraction (such as P_w) a very good analytical solution has been found. If the P availability is based on a non-water extraction, multiple regression models can be used to predict the P-AL-value. Model calculations show that environmental losses of P by leaching from the tillage layer vary from 1-2 kg ha⁻¹ a⁻¹ P at medium soil P levels to 3-15 kg ha⁻¹ a⁻¹ P at high values.

Keywords: phosphorus, phosphate, P sorption, P desorption, P availability, P accumulation, P leaching.

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Project 642

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Preface

In this report an overview is presented of results of a study carried out by DLO-Winand Staring Centre in 1997. The study was a subject of a project called 'nutrient losses from agricultural soils' (project 642) carried out by order of the nutrient programme 288 'Phosphorus dynamics and nutrient losses to groundwater and surface water' which was financially supported by the Dutch Ministry of Agriculture, Nature Management and Fisheries.

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Summary

As a result of high P application rates in the past, phosphorus soil fertility levels of agricultural land have reached high values in most areas. Since manure applications have been strongly restricted over the last decade, in order to reduce P accumulation and P leaching, farmers become more and more afraid that the soil fertility will decrease to values below acceptable levels (from an agronomic point of view). In this study, soil fertility P parameters have been related to soil chemical P parameters and P leaching. The relations are based upon results and data of other studies.

Based on the process description of P sorption and desorption kinetics, it is possible to predict a description of soil fertility P level. If the soil fertility P level is based on a *water extraction* (such as P_w), a very good prediction of this parameter is possible using the description of P reversibly bound phosphorus (analytical solution). Since, the P_w parameter is determined at a short desorption time after dilution (one hour), it is important that the decrease in adsorbed P, as a result of dilution, and the desorption time itself is taken into account (non-equilibrium situation).

For *non-water extractions* (such as P-AL) not only the amount of reversibly bound phosphorus is important but also a fraction of the amount of phosphorus which is bound at the surface of micropores. This diffundated P is considered as very insoluble, which will not desorb under normal agricultural conditions, where the amount of adsorbed P determines the P concentration in the soil solution. Therefore, the amount of diffundated P, which is extracted with a non-water extraction, is probably not available for plants. If the P availability is based on a non-water extraction, multiple regression models can be used to predict the P-AL-value.

Model calculations showed that environmental losses of P by leaching from the tillage layer to deeper layers depend on soil P level and vary in non-P saturated soils from 1-2 kg ha⁻¹ a⁻¹ P at medium soil P levels to 3-15 kg ha⁻¹ a⁻¹ P at high values.

The rate of the decrease of the soil fertility parameters is determined by the initial soil fertility value, the amount of P shortage, the sum of the amount of oxalate extractable aluminium and iron (Al+Fe)_{ox} and the precipitation surplus. The decrease in P leaching is also determined by these parameters because P concentration are determined by the soil fertility P level. For example, at a P shortage of 30 kg ha⁻¹ a⁻¹ P₂O₅, the initial P_w-value of a tillage layer (0.2 m) is reduced to 50% within 10 years, at an (Al+Fe)_{ox} content of 50 mmol kg⁻¹, and within 20 years at an (Al+Fe)_{ox} content of 110 mmol kg⁻¹. The time needed for the above mentioned 50% reduction strongly depends on the depth of the tillage layer (rootzone), which is often much thinner (0.05 m). For example, at a P shortage of 15 kg ha⁻¹ a⁻¹ P the initial P-AL-value of a tillage layer (0.05 m) is reduced to 50% within 5-10 years at an (Al+Fe)_{ox} content of 80 mmol kg⁻¹. At a tillage layer of 0.2 m the 50% reduction time is about 10-30 years (depending on the initial P-AL-value).

Since the P availability can be described by P sorption and desorption kinetics,

deterministic models can be very helpful in analyzing the nature of the surplus of P that may be needed to maintain optimum soil P levels.

1 Introduction

In the Netherlands most agricultural soils have high soil fertility levels of phosphorus (P). These high soil P levels are a result of high application rates of manure during the last 20 years, mainly in areas with intensive husbandry. In these areas the application rates of P were much higher than crop requirement. In some areas the accumulation of P in soils has caused environmental problems such as leaching of P to groundwater and surface water. In the Netherlands the contribution of agriculture on the eutrophication problem is still very high (Boers et al., 1997).

Due to legislation, P application rates have been reduced in the last decade but still exceed crop requirement. Within the forthcoming 10 years recommended P application rates should comply to crop requirements. Since a part of the annual P application rate is not available to plants (due to inorganic fixation, organic immobilisation, and leaching of P), P application levels will always exceed plant uptake.

In the past, relations between plant requirement, soil fertility levels and application rates have been extensively studied. Based on these practical 'response-curves', recommendations of P application rates have been indicated. These studies, however, do not include environmental effects such as phosphate saturation of the soil or P leaching. Other studies, with an environmental point of view, have described P leaching as a function of P-pools and associated chemical reactions. The relation between soil fertility P levels, soil P pools, in which phosphorus has accumulated, and P leaching still need to be analyzed. As a result the decrease of soil fertility P level caused by leaching of P out of the tillage layer can be estimated. In this way it is possible to give an indication of soil P levels at which sustainable agriculture is attained.

In order to assess the impact of nutrient management strategies, fertilizer recommendations and national manure policy on the change in soil P levels and P leaching in the short and long term, this study was focused on the relation between phosphate accumulation, soil P levels, and P leaching. The relations are based upon results and data of other studies (Schoumans et al., 1991; Chardon, 1994; Schoumans; 1995). These studies resulted in empirical methods to relate soil fertility parameters versus soil chemical parameters by means of linear and non-linear relations. In this study we introduce a more soil chemical approach. The research has been restricted to non-calcareous sandy soils because for those soils information was available and these soils are a major source of the eutrophication problem in the Netherlands.

In chapter 2 a short overview of the phosphate reactions in soil is given together with the model description for these reactions. If soil P levels are based on water soluble phosphate, equations, to relate soil P levels to soil P pools, can be derived from the model description (chapter 3; deterministic approach). For other P extractions methods a different approach is used. In chapter 4 the effect of leaching of P on the decrease of soil P fertility parameters is described and modelled. In

chapter 5 conclusions are formulated with respect to the relations between phosphate accumulation, soil P levels, and P leaching.

2 Phosphate reactions and model description

2.1 Phosphate reactions

In soils phosphate can react with:

- micro-crystalline or amorphous Al- en Fe-(hydr)oxides,
- complexes of Al en Fe and organic matter,
- edges of clay minerals,
- Al- en Fe-(hydr)oxides bound at the surface of clay minerals,
- calcium or magnesium carbonates (lime).

In non-calcareous sandy soils the main reactive components are micro-crystalline or amorphous Al- en Fe-(hydr)oxides and probably also complexes of organic matter with Al or Fe.

With respect to the reaction of phosphate with the amorphous Al- en Fe-(hydr)oxides there is a distinction between a fast adsorption reaction at the surface of the Al- en Fe-(hydr)oxides (< 1 day) (Breeuwsma, 1973: hematite; Van Riemsdijk, 1979: gibbsite) and a slow diffusion reaction of phosphate into the Al- en Fe-(hydr)oxides (Van Riemsdijk, 1979; Barrow, 1983; van der Zee, 1988). The surface reaction is described as ligand change between phosphate anions and OH or OH₂-groups at the surface sesquioxides (Atkinson et al., 1972; Breeuwsma, 1973; Parfitt et al., 1975 and 1977). The description of the diffusion process is not clear. Van Riemsdijk (1979) and Barrow (1983) described the diffusion as a slow transport of phosphate through the solid phase followed by a fast precipitation reaction. Madrid and De Arambarri (1985) and Willett et al. (1988) describe the reaction as a slow diffusion of phosphate through the micropores followed by a fast adsorption reaction. Van der Zee (1988) assumed that a precipitation reaction takes place in the micropores. An overall consensus has been established with the idea that the main time dependent step is the diffusion reaction of phosphate into the aggregates, which has to take place before any reaction of phosphorus with Al- and Fe-(hydr)oxides could take place.

The surface adsorption reaction of phosphate is considered as a completely reversible reaction. Phosphate which has been transported into the aggregates of Al- and Fe-(hydr)oxides is stable and is considered as 'irreversibly' bound phosphate with respect to agricultural circumstances (Van der Zee, 1988). Lookman (1995) showed that at low P concentrations ('zero') also the 'irreversibly bound' phosphate will be released.

The reaction of phosphate with organic matter is seen as a reaction of phosphate with positive charged Al/Fe-chelates (Al/Fe-organic matter structures) (Williams, 1960; Dormaar, 1963; Anderson et al., 1974; Appelt et al., 1975). This phosphate reaction is considered as a completely reversible phosphate reaction (Schoumans, in prep.).

2.2 Model description

2.2.1 Phosphate adsorption

The adsorption reaction of phosphate at the surface of Al- and Fe(hydr)oxides and the reaction of phosphate with the chelates is considered as a fast *reversible* reaction. These type of reactions are often described by the Langmuir equation because the adsorption reactions are controlled by a maximum (Van der Zee, 1988; Schoumans, 1995).

$$\frac{dQ}{dt} = k_a c (Q_m - Q) - k_d Q \quad (1)$$

Q	= amount P adsorbed	(mmol kg ⁻¹ P)
k_a	= adsorption constant	(m ³ mol ⁻¹ h ⁻¹)
k_d	= desorption constant	(h ⁻¹)
c	= concentration of P	(mol m ⁻³)
Q_m	= maximum amount of P which can be adsorbed	(mmol kg ⁻¹ P)

At equilibrium ($dQ/dt=0$) equation (2) is valid:

$$Q = \frac{K c Q_m}{1 + K c} \quad (2)$$

$$K = k_a/k_d = \text{adsorption constant} \quad (\text{m}^3 \text{mol}^{-1})$$

For non-calcareous sandy soils Van der Zee (1988) found:

$$10 < K < 100$$

and

$$Q_m \approx \frac{1}{6} (Al + Fe)_{ox} \quad (3)$$

where

$$Al_{ox} + Fe_{ox} = \text{sum of the amount of oxalate extractable Al and Fe} \quad (\text{mmol kg}^{-1})$$

According to Schwertmann (1964) the amount of oxalate extractable Al and Fe is a measure for the total amount of all non-crystalline Al and Fe fractions in soils.

2.2.2 Phosphate diffusion

For the 'irreversible' phosphate diffusion reaction (S) a different process description has been published. Van der Zee (1988) and Van der Zee et al. (1990a) used equations based on the exposure integral e.g.:

$$S = \sum_{j=1}^n a_j (ct)^{j/2} \quad (4)$$

$$S = \sum_{j=1}^n a_j \ln(I) \quad (5)$$

$$S = \frac{S_m}{1 + B_s I^{-K_s}} = S_m \frac{(I)^{K_s}}{(I)^{K_s} + B_s} \quad (6)$$

S	= amount of P diffundated into aggregates	(mol kg ⁻¹)
S_m	= maximum amount of P diffundated into aggregates	(mol kg ⁻¹)
I	= exposure integral	(-)
	= $\gamma \int (c - c_e) dt$	
γ	= parameter making I dimensionless	(mol ⁻¹ m ³ d ⁻¹)
c	= concentration of P	(mol m ⁻³)
c_e	= minimum concentration of P after which phosphate diffusion can take place	(mol m ⁻³)
t	= reaction time	(d)
B_s	= sorption constant	(-)
K_s	= sorption constant	(-)
j	= number of different adsorption sites	(-)

The problem with equation (5) and (6) is that S is not defined for negative values of I . The value of I is negative for desorption situations ($c < c_e$). So mathematically all phosphate is 'irreversibly bound'. Lookman (1995) showed that in the long term all phosphate will be desorbed. Therefore, in the nutrient model ANIMO (Groenendijk and Kroes, 1997; Groenendijk, in prep.) a process formulation is used at which desorption of the 'irreversible pool' can take place (equation 7). The parameter values of this diffusion reaction have been derived for sorption situations (batch experiment; Schoumans, 1995). For desorption situation ($K_i C^{N_i} < S_i$) the desorption rate of the 'irreversible' bound pool is assumed 1/100 of sorption rate (α_i).

$$\frac{dS}{dt} = \sum_{i=1}^n \alpha_i (K_i C^{N_i} - S_i) \quad (7)$$

When equilibrium is reached ($dS/dt=0$) equation (7) becomes:

$$S_m = \sum_{i=1}^n K_i C^{N_i} \quad (8)$$

N_i = Freundlich exponent of pool i (-)

In non-calcareous sandy soils Van der Zee (1988) found:

$$S_m \approx \frac{1}{3} (Al + Fe)_{ox} \quad (9)$$

$Al_{ox} + Fe_{ox}$ = sum of the amount of oxalate extractable Al en Fe (mmol kg⁻¹)

The reversible and 'irreversible' sorption processes have been used in defining the so called 'phosphate saturated soils' (Van der Zee, 1988). For sandy districts in the Netherlands these soils have been identified by Reijerink and Breeuwsma (1992).

2.2.3 Phosphate sorption

The total amount of phosphate sorption (F) can be calculated from the sum of adsorbed P (Q) and diffundated P (S):

$$\frac{dF}{dt} = \frac{dQ}{dt} + \frac{dS}{dt} \quad (10)$$

Since the adsorption reaction (Q) is a fast reaction equilibrium is reached within 1 day. After this reaction time the amount of adsorbed P is described by the Langmuir equation (Eq. 2) and depends of the phosphorus concentration (Fig. 1). The total amount of sorbed P depends on the amount of adsorbed P (Q) and the amount of diffundated P (S). This diffusion reaction is a slow reaction which increases with the reaction time (S₁ to S₄; Fig. 1). Therefore, the total sorption reaction increases (from F₁ to F₄) according as the reaction time increases.

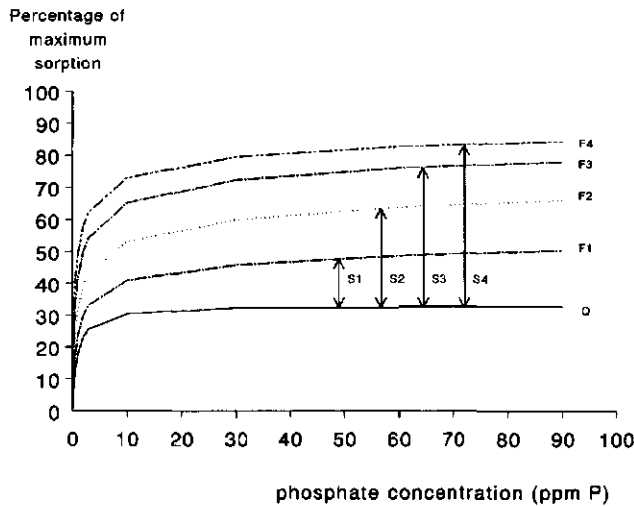


Fig. 1 Qualitative description of the effect of concentration of P and reaction time on P sorption (Q=adsorption process, S=diffusion process, F=total sorption).

At equilibrium (dF/dt=0) the maximum amount of P sorption is given by equation (3) and (8):

$$F_{\max} = Q_{\max} + S_{\max} = \frac{1}{6} (Al+Fe)_{ox} + \frac{1}{3} (Al+Fe)_{ox} = 0.5 (Al+Fe)_{ox} \quad (11)$$

F_{\max}	= maximum amount of P sorption	(mmol kg ⁻¹)
Q_{\max}	= maximum amount of P adsorption	(mmol kg ⁻¹)
S_{\max}	= maximum amount of P diffusion	(mmol kg ⁻¹)
$Al_{ox} + Fe_{ox}$	= sum of the amount of oxalate extractable Al en Fe	(mmol kg ⁻¹)

Schoumans et al. (1986) found similar relation. The ratio of F_m (PSC; total phosphate sorption capacity) and the sum of Al_{ox} and Fe_{ox} had a value of 0.52 (fig. 2). If they used linear regression analysis between F_m and Al_{ox} and Fe_{ox} they found an intercept of 4.6 and a coefficient of 0.39 (fig. 2).

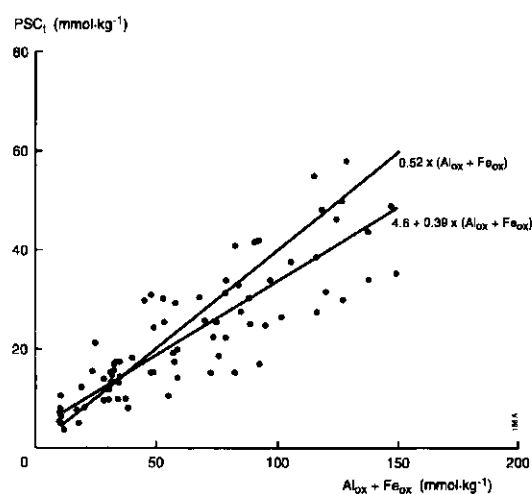


Fig. 2 The relationship between oxalate extractable Al and Fe and the total P sorption capacity (PSC= F_{\max}) according to Schoumans et al. (1986)

3 Modelling P availability

In Dutch agriculture two soil tests are used for P recommendations. For pasture ammonium lactate solution is applied (P-AL-value; Égner et al., 1960). This is a method to determine the capacity of the soil to release P in the long term (capacity parameter). For arable land a water extraction is applied in order to predict the amount of P which is directly available for crops (intensity parameter; Pw-value). In other countries in Western Europe water extractable P tests are not currently used. As capacity parameter for phosphorus a lot of methods are used such as P-Olsen (England, Spain), P-Morgan (Ireland, Scotland), P-Hebert/Jouet (France), P-Double Lactate (DL; Germany). In Europe the CaCl_2 solution will probably be introduced as a standard for the determination of P availability in the near future. In this study only Pw- and P-AL-value will be related to the kinetics of phosphate in non-calcareous sandy soils (paragraph 3.3 Pw-value and paragraph 3.4 P-AL-value and P-Olsen). First of all the results of simple regressions methods, which have been published by Schoumans et al. (1991) and Chardon (1994), will be discussed (paragraph 3.2).

3.1 P soil tests

Pw-value

The Pw-value is determined at a soil-solution ratio of 1:60 (v/v). The method is fully described by Sissingh (1971). In practice about 1.2 ml soil is incubated together with 2 ml water for 20 hours. After incubation 70 ml water is added and the soil suspension is shaken for 1 hour. After filtration the P concentration is measured in the filtrate. The Pw-value is expressed in mg P_2O_5 per liter soil.

P-AL-value

The P-AL-value is determined at a soil-solution ratio of 1:20 (w/v). The method is fully described by Égner et al. (1960), 2.5 g of soil is shaken together with 50 ml ammoniumlactate-acetic-acid solution (pH 3.75) for a period of 4 hours. The amount of P in the extract is determined. The P-AL-value is expressed in mg P_2O_5 per 100 gram soil.

P-Olsen

The P-Olsen-value is determined at a soil-solution ratio of 1:20 (w/v). The method is fully described by Olsen and Sommers (1982), 5 g of soil is shaken together with 100 ml sodium bicarbonate solution (pH 8.5) for a period of 30 minutes. The amount of P in the extract is determined. The P-AL-value is expressed in mg P per kg soil.

3.2 Regression models

Soil fertility parameters and soil P pools can be related by regression analysis (linear as well as non-linear). Lexmond et al. (1982) measured Pw-values in 84 soil samples and the total amount of sorbed P ($F_o = P_{ox}$; by means of an oxalate extraction according

to Schwertmann (1964)). Furthermore oxalate extractable Al and Fe was determined because P sorption depends on oxalate extractable Al and Fe. Chardon (1994) measured P_w-value, P_{ox}, Fe_{ox}, and Al_{ox} in 98 soil samples. Schoumans et al. (1991) measured P_w-values, P-AL-values, reversibly adsorbed P (Q₀=P_i; by means of P-iron method according to Van der Zee (1988)) and total sorbed P (P_{ox}, Al_{ox} and Fe_{ox}) in 74 soil samples.

P_w-value

The P_w-method extracts only a small part of the total amount of sorbed P. If both values are expressed in the same unit (e.g. mmol P per kg soil) Schoumans et al. (1991) calculated a mean ratio between P_w and P_{ox} of approx. 4%:

$$\left(\frac{P'_w}{P_{ox}} \right) * 100\% = 4.0 \pm 2.7\% \quad (12)$$

Lexmond et al. (1982), Chardon (1994) and Schoumans et al. (1991) used the same equation to fit P_w-value:

Lexmond et al. (1982):

$$P_w = 429 * \left(\frac{P_{ox}}{Al_{ox} + Fe_{ox}} \right)^{1.20} \quad n = 84 \quad (13)$$

Chardon (1994):

$$P_w = 633 * \left(\frac{P_{ox}}{Al_{ox} + Fe_{ox}} \right)^{1.96} \quad n = 98 \quad r^2 = 0.86 \quad (14)$$

Schoumans et al. (1991):

$$P_w = 468 * \left(\frac{P_{ox}}{Al_{ox} + Fe_{ox}} \right)^{1.55} \quad n = 74 \quad V^2 = 63.2 \quad (15)$$

According to Schoumans et al. (1991) there is statistically no difference between equation (15) and a simple linear relationship:

$$P_w = -36.66 + 397.9 * \left(\frac{P_{ox}}{Al_{ox} + Fe_{ox}} \right) \quad n = 74 \quad V^2 = 65.4 \quad (16)$$

All studies led to the conclusion that the prediction of P_w-value based on the phosphate saturation index ($PSI = P_{ox} / (Al_{ox} + Fe_{ox})$) is rather poor. Most probably this is due to the poor solubility of the major part of P_{ox} ('irreversibly' bound P). A better relationship could be expected when the P_w-value is fitted to the amount of P that is reversibly adsorbed (P_i) (Schoumans et al., 1991). The equation of the fitted line is:

$$P_w = -38.36 + 22.35 * P_i \quad n = 74 \quad V^2 = 65.4 \quad (17)$$

The percentage variance accounted for (V²) in eq. (7) is not much higher than the percentage variance accounted for in the equations based on PSI (equations 12-15). The relation between P_w and P_i shown in figure 3 is curvilinear. Non-linear relationships between P_w and P_i were not fitted in this study. The standard error of the prediction of the P_w-value will still be high (fig. 3).

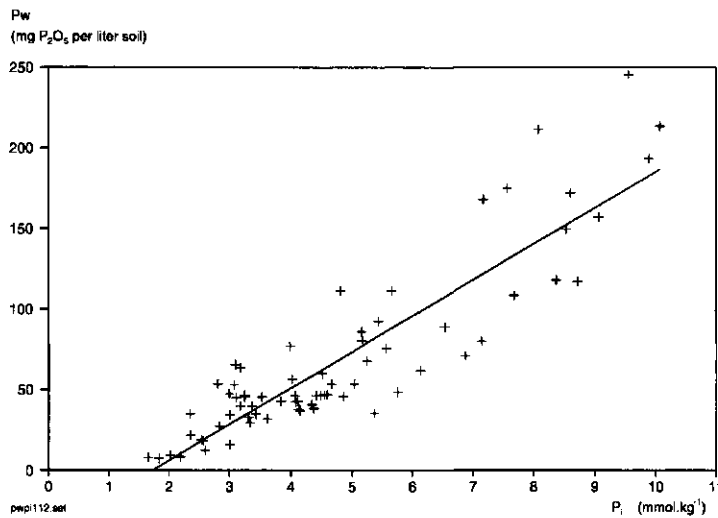


Fig. 3 Relationship between P_w-value and adsorbed P (P_i method) (Schoumans et al., 1991)

P-AL-value

The amount of P determined by the P-AL-method is about 50% of total sorbed P (expressed in mmol kg⁻¹) (Schoumans et al., 1991). This is twice as high as the reversibly bound P (P_i):

$$\left(\frac{P'_{al}}{P_{ox}} \right) * 100\% = (54.7 \pm 13.7)\% \quad (18)$$

$$\left(\frac{P_i}{P_{ox}} \right) * 100\% = (28.4 \pm 9.2)\% \quad (19)$$

Furthermore, a good relationship between the P-AL-value and reversibly adsorbed P (P_i) was found (Fig. 4) (Schoumans et al., 1991).

$$P\text{-AL-value} = 14.1 * P_i \quad n = 74 \quad V^2 = 89.6 \quad (20)$$

By definition these relationship don't have to be causal. They represent a static description of the status of the samples. Thus, it remains uncertain whether the P-AL-value of a soil decreases according to the fitted line if the amount of adsorbed P (P_i) in this soil decreases as a result of e.g. P leaching. Therefore, a modelling approaches is required.

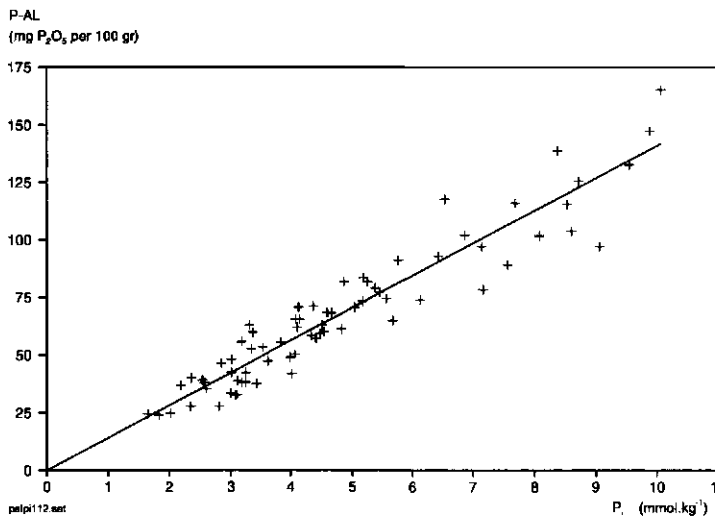


Fig. 4 Relationship between the P-AL-value and adsorbed P (P_i) (according to Schoumans et al., 1991)

3.3 Prediction of water extractable P: a deterministic approach

As an alternative to the above mentioned regression analysis, the amount of directly available water-soluble P, such as Pw-value, can be calculated from the Langmuir equation (Schoumans, 1995).

desorption of P from the soil = increase of P in solution

$$(Q_o - Q_e) \cdot \rho_d \cdot V_{soil} \cdot M_p = C_e \cdot V_w \cdot 10^3 \quad (21)$$

Q_o	= amount of adsorbed P at the start of Pw-method	(mmol kg ⁻¹)
Q_e	= amount of adsorbed P after desorption at the end of the Pw-method	(mmol kg ⁻¹)
ρ_d	= bulk density	(kg m ⁻³)
V_{soil}	= volume of soil sample = $1.2 \cdot 10^{-6}$	(m ³)
V_w	= volume water used by the Pw-method = $72 \cdot 10^{-6}$	(m ³)
M_p	= molweight of phosphorus = 31	(mg mmol ⁻¹)
C_e	= equilibrium P concentration in solution	(mg l ⁻¹)
10^3	= factor depending on the used unities	(l m ⁻³)

The Langmuir equation (2) can be substituted in equation (21) if an equilibrium between adsorbed and soluble P is assumed in the Pw method:

$$Q_o - \frac{K C_e Q_m}{1 + K C_e} = \frac{1935.5}{\rho_d} C_e \quad (22)$$

The P concentration measured at the end of the Pw-method (C_{Pw}) will be lower than the equilibrium concentration (C_e) when equilibrium is not reached, within 1 hour. In this case equation (22) becomes:

$$Q_o - \frac{K f C_{Pw} Q_m}{1 + K f C_{Pw}} = \frac{1935.5}{\rho_d} f C_{Pw} \quad (23)$$

where

$$f = C_e / C_{Pw} > 1$$

$$C_{Pw} = \text{P concentration measured at the end of the Pw-method} \quad (\text{mg.l}^{-1} \text{ P})$$

The Pw-value is calculated from the P concentration measured at the end of the Pw-method (C_{Pw}):

$$P_w = 137,42 C_{Pw} \quad (24)$$

P_w = directly available water soluble P in soil (mg P₂O₅ per 1 soil)

Substitution of equation 24 and $Q_m = \beta (Al+Fe)_{ox}$ (see equation 3) in (23) result in:

$$Q_o - \frac{\alpha_o P_w}{1 + \alpha_1 P_w} = \alpha_2 P_w \quad (25)$$

$$\alpha_o = K f 7.277 \cdot 10^{-3} \beta (Al + Fe)_{ox}$$

$$\alpha_1 = K f 7.277 \cdot 10^{-3}$$

$$\alpha_2 = 14.08 f / \rho_d$$

$$P_w = \frac{-a_1 + \sqrt{a_1^2 - 4 a_o a_2}}{2 a_o} \quad (26)$$

$$a_o = \alpha_1 \alpha_2$$

$$a_1 = \alpha_2 + \alpha_o - \alpha_1 Q_o$$

$$a_2 = -Q_o$$

Pw-value, P_{ox} , Al_{ox} , Fe_{ox} , Q_0 , and the equilibrium soil solution concentration of P (c_{des}) were measured from soil samples taken at nine locations from the upper 0.4m of the soil profile (two layers; 0-0.2 m and 0.2-0.4 m) (Schoumans, 1995). The c_{des} concentration was determined after 1 week at a soil solution ratio of 1:10. After the determination of c_{des} the (filtered) soil sample was used to determine Q_0 . In this study Q_0 was not corrected for the amount of P already desorbed at the determination of c_{des} (error less than 10%). From the relationship between Pw and c_{des} the parameters of the Langmuir equation were assessed ($K=31 \text{ m}^3 \text{ mol}^{-1}$ and $Q_m = 0.19 (Al_{ox} + Fe_{ox})$) using Eq. 25. The prediction of the Pw-value is made with $f=1$ (assuming equilibrium between the adsorbed P at the surface and the P concentration in solution at the end of the Pw-method). Figure 5 shows the relation between the Pw-value (measured and predicted) and c_{des} for these soil samples.

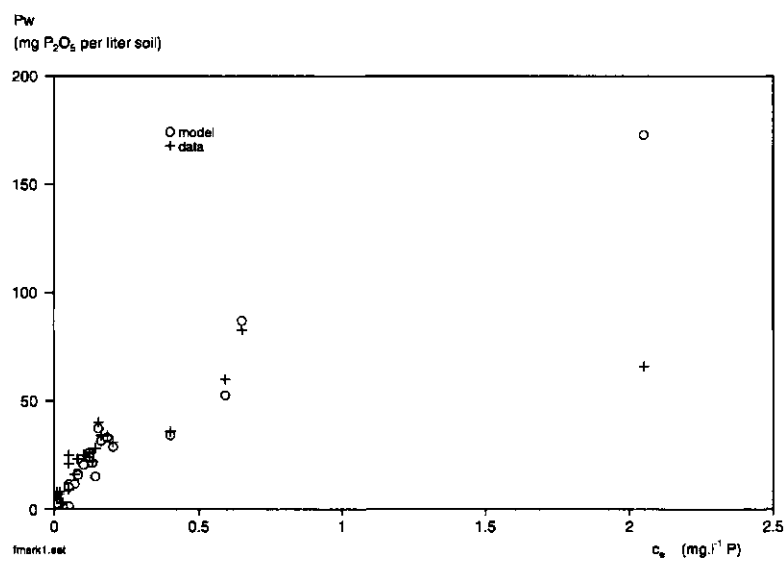


Fig. 5 Measured (+) and predicted (o) Pw-value as a function of P equilibrium concentration (c_{des}) (Schoumans, 1995)

At low c_{des} concentrations a relation between predicted and measured Pw-value can be established. Unfortunately at high concentrations only one value is available. However, the difference between the measured value and predicted value is large under these circumstances. The soil chemical parameters and soil fertility parameters of this soil sample were re-analyzed but no differences were found. In order to predict these Pw-values, equilibrium was assumed between the amount of P adsorbed at the soil particles and the P concentration of the solution at the end of the Pw-method ($f=1$ in equation 26) (Schoumans, 1995). If this assumption is not valid a new equation can be derived, assuming that:

desorption of P from the soil = increase of P in solution

$$\frac{dQ}{dt} \rho_d V_{ground} M_p = - \frac{dc}{dt} V_{H_2O} 10^3 \quad (27)$$

$$y \frac{dQ}{dt} = - \frac{dc}{dt} \quad (28)$$

$$y = \frac{V_{ground} M_p \rho_d}{V_w 10^3} = \frac{1.2 \cdot 31 \cdot 1300}{72 \cdot 10^3} = 0.67167 \quad (29)$$

$$y \int_{t=0}^{t=t} (k_a c (Q_m - Q) - k_d Q) dt = - \int_{c=c_1}^{c=c_2} dc \quad (30)$$

Equation (30) can be rewritten to:

$$y \int_{t=0}^{t=t} (a c - b) dt = - \int_{c=c_1}^{c=c_2} dc \quad (31)$$

with

$$a = k_a (Q_m - Q)$$

$$b = k_d Q$$

and assuming that changes in the adsorbed amount Q are negligible.

The integral of Eq (31) gives:

$$- y t = \frac{1}{a} \ln \left(\frac{a c_2 - b}{a c_1 - b} \right) \quad (32)$$

$$c_2 = \frac{b}{a} + \left(c_1 - \frac{b}{a} \right) e^{-a y t} \quad (33)$$

At t=0 and t=∞ c₂ becomes

$$t=0 \quad : c_2 = c_1$$

$$t=\infty \quad : c_2 = b/a$$

Furthermore, the value of b/a is equivalent with

$$\frac{b}{a} = \frac{k_d Q}{k_a(Q_m - Q)} = \frac{Q}{K(Q_m - Q)} = c_e \quad (34)$$

At the determination of the Pw-value 1.2 ml soil is incubated for 20 hours with 2 ml water. After these 20 hours 70 ml water is added. It is valid to assume that in the first 20 hours equilibrium is reached between the surface and the solution (c_e). When after the incubation period 70 ml of water is added, the initial P concentration (c_i) is reduced by a factor 36 (from 2 ml to 72 ml):

$$c_i = c_e / 36 = (b/a) / 36$$

$$c_2 = \frac{b}{a} \left(1 + \left(\frac{1}{36} - 1 \right) e^{-ayt} \right) \quad (35)$$

$$\frac{c_t}{c_e} = \left(1 - 0.9722 e^{-ayt} \right) \quad (36)$$

$$\frac{c_t}{c_e} = \left(1 - 0.9722 e^{-Kk_d(Q_m - Q)yt} \right) \quad (37)$$

$$\frac{c_t}{c_e} = \left(1 - 0.9722 e^{-Kk_d(1 - Q/Q_m)ytQ_m} \right) \quad (38)$$

The Pw-value is measured after shaking the diluted suspension (72 ml) for 1 hour ($c_i = c_{1 \text{ hour}}$):

$$\text{Pw-value} = 137.42 * C_{1 \text{ hour}} \quad (\text{mg P}_2\text{O}_5/\text{l soil})$$

$$\text{Pw-value} = \frac{Q/Q_m}{K(1 - Q/Q_m)} \cdot \lambda_{\text{corr}} \cdot 137.42 \quad (39)$$

where

$$\lambda_{\text{corr}} = \left(1 - 0.9722 e^{-Kk_d(1 - Q/Q_m)ytQ_m} \right) \quad (40)$$

If the amount of adsorbed P does not decrease, equation (39) is valid (assumption made by equation 31). For example, if the Pw-method was carried out at $t=\infty$ (and not $t=1$ hour), λ_{corr} will become 1 and the final P concentration is fully determined by the initial amount of adsorbed P according to the Langmuir equation ($c_e = Q/K(Q_m - Q)$); equation

39). Figure 6 shows that no equilibrium is reached at the Pw-method, mainly at high desorption fractions in soil samples (Q/Q_m). A high desorption fraction indicates high P equilibrium concentrations (c_e) in the soil solution (eq. 39). The relation between this equilibrium concentration and the relative P concentration (c_1/c_e) and the Pw-value is shown in figure 7.

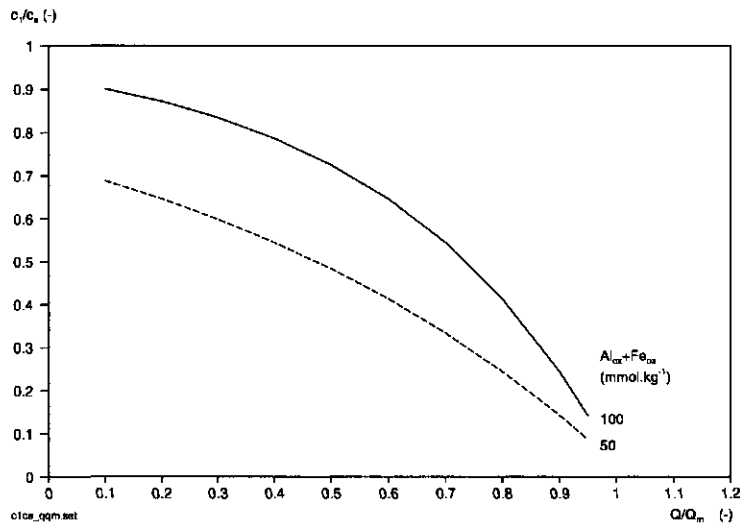


Fig. 6 The effect of the desorption fraction on the P concentration ratio (P concentration after 1 hour and the equilibrium concentration) at two $Al_{ox}+Fe_{ox}$ levels

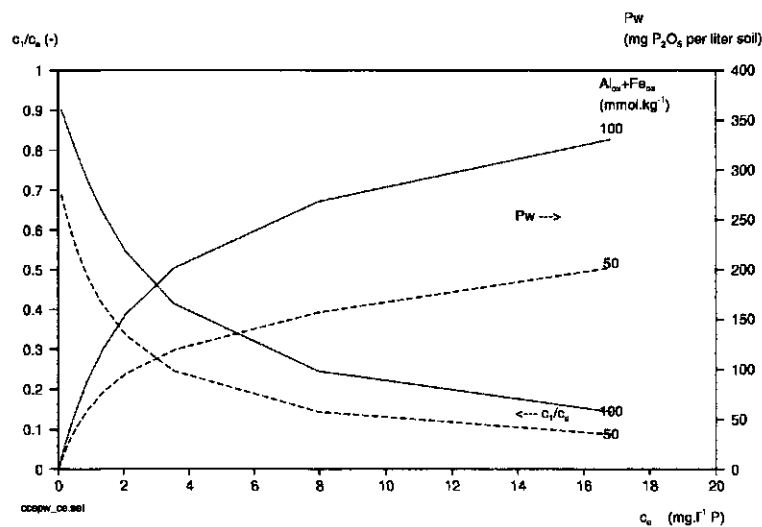


Fig. 7 The effect of P equilibrium concentration on the relative P concentration (P concentration after 1 hour and the equilibrium concentration) and the Pw-value at two $Al_{ox}+Fe_{ox}$ levels

Figure 6 and 7 are only valid if the decrease in Q is assumed nil during the Pw-method.

If the decrease in Q is taken into account an analytical solution is possible assuming that the sum of adsorbed P and P in solution ($Q_T = Q + c/\gamma = Q + \alpha c$) is constant (De Willigen, P., 1997, AB-DLO, pers. comment). Substitution in equation 30 result in:

$$y \int_{t=0}^{t=\tau} (k_a c (Q_m - (Q_T - \alpha c)) - k_d (Q_T - \alpha c)) dt = - \int_{c=c_1}^{c=c_2} dc \quad (41)$$

Re-arranging:

$$\alpha \frac{dc}{dt} = k_d Q_T + (-k_a (Q_m - Q_T) - \alpha k_d) c - k_a c^2 \quad (42)$$

If

$$a_2 = -k_a \alpha$$

$$a_1 = -k_a (Q_m - Q_T) - k_d \alpha$$

$$a_0 = +k_d Q_T$$

Then equation 42 becomes:

$$\int_{c_1}^{c_2} \frac{dc}{(a_0 + a_1 c + a_2 c^2)} = y \int_{t=0}^{t=\tau} dt \quad (43)$$

Assume $D = a_1^2 - 4 a_0 a_2$ and $D > 0$ then the solution of 42 becomes:

$$\left[\frac{1}{\sqrt{D}} \ln \frac{2 a_2 c + a_1 - \sqrt{D}}{2 a_2 c + a_1 + \sqrt{D}} \right]_{c=c_1}^{c=c_2} = y [t]_{t=0}^{t=\tau} \quad (44)$$

So,

$$\frac{1}{\sqrt{D}} \ln \left(\frac{2 a_2 c_2 + a_1 - \sqrt{D}}{2 a_2 c_2 + a_1 + \sqrt{D}} \cdot \frac{2 a_2 c_1 + a_1 + \sqrt{D}}{2 a_2 c_1 + a_1 - \sqrt{D}} \right) = y t \quad (45)$$

The solution of c_2 is:

$$c_2 = \frac{(a_1 - \sqrt{D}) - (a_1 + \sqrt{D}) \tau}{2 a_2 (\tau - 1)} \quad (46)$$

$$\begin{aligned}
a_2 &= -k_a \alpha \\
a_1 &= -k_a (Q_m - Q_T) - k_d \alpha \\
a_0 &= +k_d Q_T \\
\alpha &= 1/y \\
y &= V_{soil} M_p \rho_d / (V_{H2O} 10^3) \\
&= 1.2 \cdot 31 \cdot 1300 / (72 \cdot 10^3) = 0.6716666 \\
\tau &= p e^{y \sqrt{D}} \\
p &= (2 a_2 c_1 + a_1 - \sqrt{D}) / (2 a_2 c_1 + a_1 + \sqrt{D}) \\
D &= a_1^2 - 4 a_2 a_0 \\
t &= 1 \\
c_1 &= Q_T / (36 K (Q_m - Q_T))
\end{aligned}$$

So, P_w becomes

$$P_w = 137.42 C_2 \quad (47)$$

This method can momentarily be seen as the third and best method to estimate the P_w -value. The assumption made in the first method in equation 26 (method I) is that equilibrium is reached. The change of adsorbed P is taken into account (Q variable). The assumption in the second method in equation 39 (method II) is that the decrease in adsorbed P is negligible (Q constant). The fact that no equilibrium is reached is taken into account. In the third method no assumptions are made (Q decreases and no equilibrium is reached). The difference between these three methods are shown in figure 8 for two levels of $Al_{ox}+Fe_{ox}$ (50 and 100). The differences are greater if the desorption fraction Q/Q_m increases.

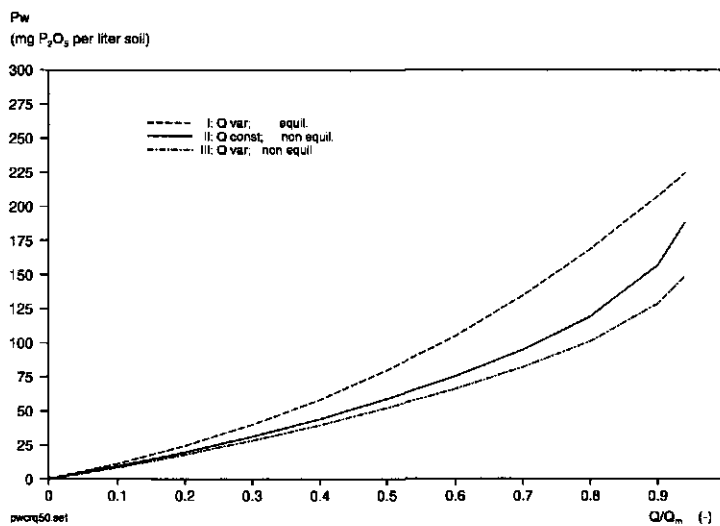


Fig. 8a The difference between three methods to predict P_w in relation to the desorption fraction (Q/Q_m) and an $Al_{ox}+Fe_{ox}$ content of 50 mmol kg^{-1}

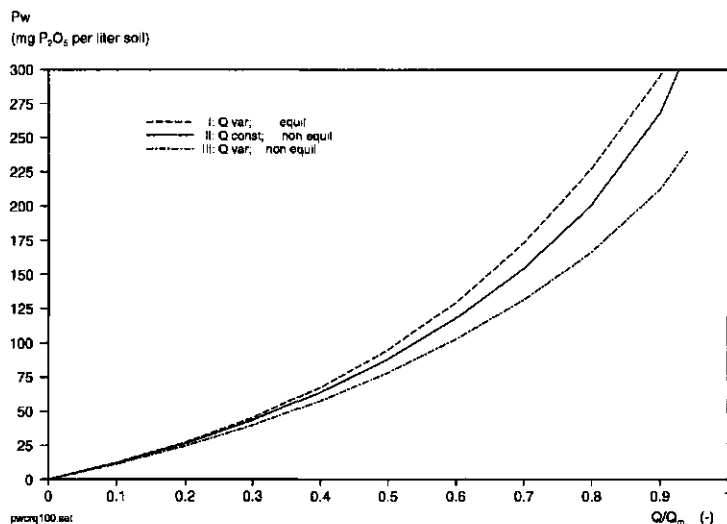


Fig. 8b The difference between three methods to predict P_w in relation to the desorption fraction (Q/Q_m) and an $Al_{ox}+Fe_{ox}$ content of 100 mmol kg^{-1}

To evaluate the applicability of method III, predicted P_w -values are compared with measured values (Fig. 9), using the same dataset as in figure 5 (Schoumans, 1995). In order to minimize all possible errors also the correction of Q_0 with respect to the amount of P already desorbed at the determination of c_{des} (fault less than 10%) has been taken into account.

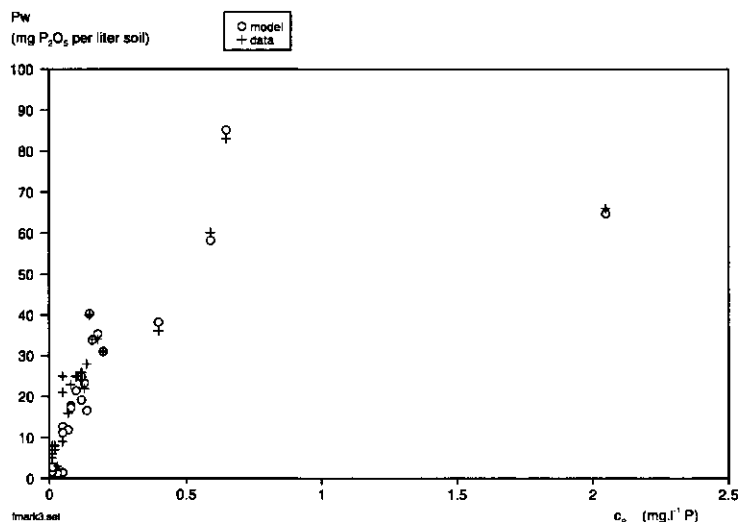


Fig. 9 Measured (+) and predicted (o) P_w -values (method III) as a function of P equilibrium concentration (c_e)

Figure 9 shows that at a mean value of $K=33 \text{ m}^3 \text{ mol}^{-1}$ and $\beta=0.1645$ (-) all measured data can be well predicted. In the Dutch protocol determination of a 'phosphate saturated soil' a K value of $35 \text{ m}^3 \text{ mol}^{-1}$ and β value of 0.167 (-) is used. The fitted parameters are in agreement with these values.

The data of Schoumans et al. (1991) are also used to test the reliability of method III. Using the parameters of the protocol a reasonable result is achieved (fig. 10).

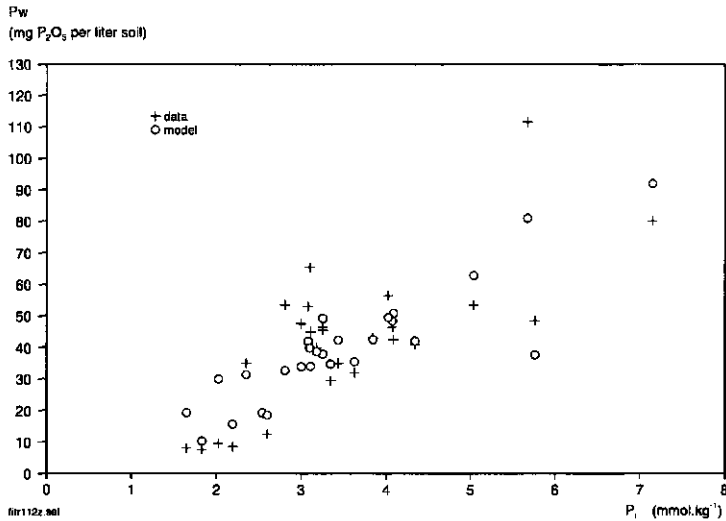


Fig. 10 Measured (+) and predicted (o) Pw-values (method III) as a function of adsorbed P (P_i)

As a result of the good reliability of method III the soil fertility parameter Pw can be predicted by the soil chemical parameters Q/Q_m and $Al_{ox}+Fe_{ox}$. Figure 11 shows which soil chemical P circumstances are necessary in order to obtain a certain (critical) Pw-value.

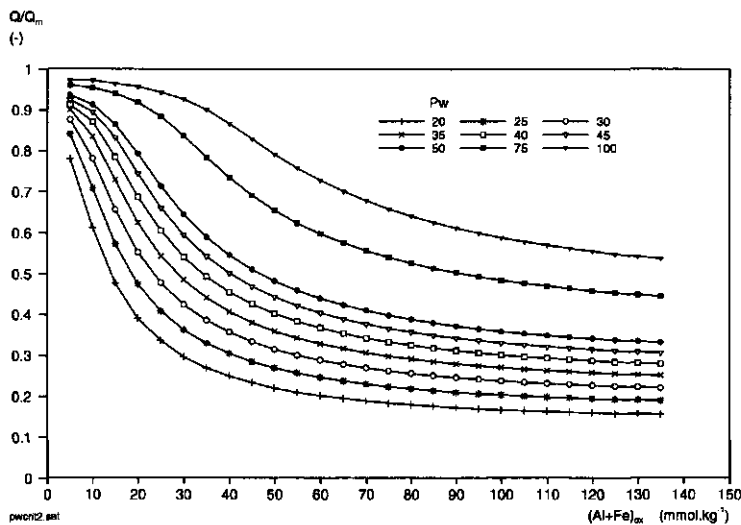


Fig. 11 Relation between the sum of oxalate extractable Al and Fe and the desorption fraction of the soil in order to obtain a certain (critical) Pw-value

3.4 Prediction of non-water extractable P: a semi-deterministic approach

In paragraph 3.2 is shown that the P-Al-value can be predicted by means of a regression model (e.g. a model based on the amount adsorbed P). The amount of P extracted with this ammonium lactate solution is on average twice as high as the amount of P which is reversibly bound (P_i ; amount of adsorbed P). This implicates that a great part of the

'irreversibly' bound P (P diffundated in the micropores of the soil aggregates) is extracted the P-AL-method. The amount of 'irreversibly' bound P in a soil sample is dependent of the manure management of the site in the past (the development of P concentration in time; equation 4-7). In situations of low P applications rates, e.g. lower than crop requirement, the P-AL-value will decrease as a result of P leaching and plant uptake. Since, the uptake of P by plants is determined by P diffusion through the soil solution to the roots (De Willigen and Van Noordwijk, 1987), the amount of adsorbed P in the soil is reduced in order to fill up the gap between P application rate and crop requirement. A laboratory experiment has been carried out in order to determine the influence of decre in the amount of adsorbed P on the P-AL-value. In two sandy, one clay and one peat soil sample the amount of adsorbed P has been decreased by means of iron papers (P_i -method). The contact time of the iron papers with each soil sample was varied from 1 to 48 hours. After desorption the P-AL-value was determined. In figure 12 the increase of P desorption and decrease of P-AL-value is shown as a function of contact time with iron paper. Both P parameters has been expressed in mmol kg^{-1} .

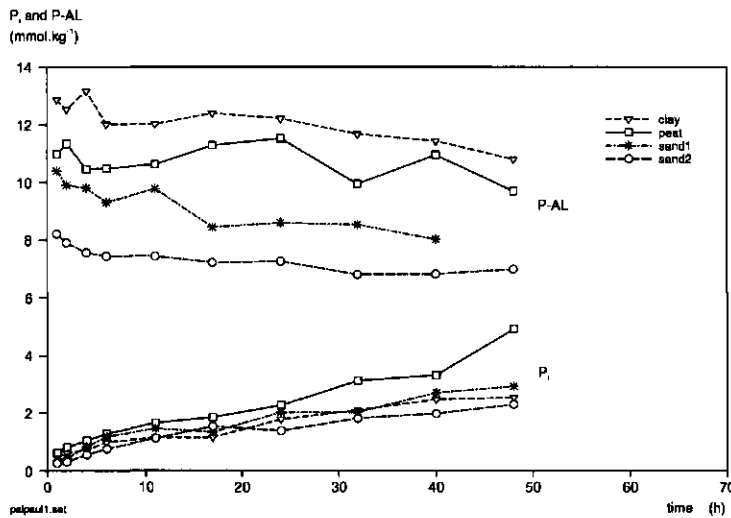


Fig. 12 The effect of contact time of the soil sample with iron paper on the amount of desorbed P (P_i) and the P-AL-value.

The decrease in P-AL-value, for the two sandy soils samples and the clay soil sample, is completely caused by the increase of the amount of desorbed P (P_i) because the sum of these two P-values is constant (fig. 13). The increase of the amount of ammonium lactate extractable P in the peat sample is maybe caused by contamination of the iron paper with small peat particles.

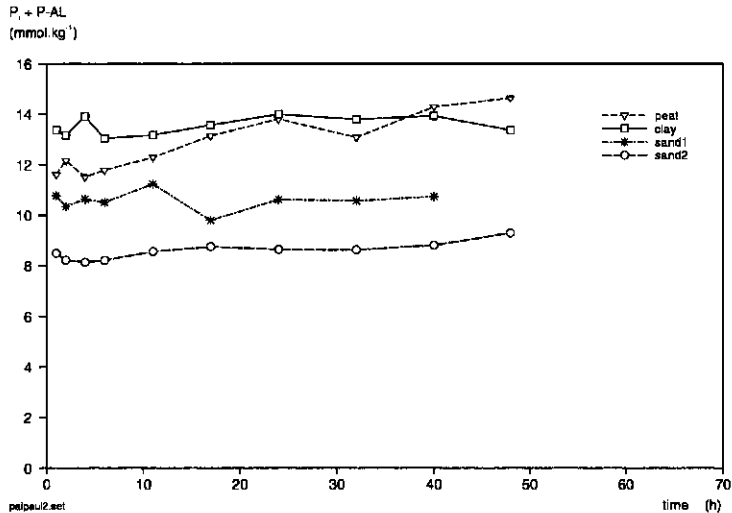


Fig. 13 The sum of P_i and P-AL as a function of the contact time of the soil sample with iron paper

The decrease in P-AL-value is fully caused by the decrease of the amount of adsorbed P. As a result the decrease of P-AL caused by P leaching or shortage of P applications can be predicted. In paragraph 3.2 the relation between the P-AL-value and adsorbed P has been described by a linear regression model. Since, some of the soil samples of this data set contain relative high amount of organic material, regression analysis has been carried out without these soil samples, because it is not sure that in peaty soil samples the decrease in P-AL can be explained by the decrease in adsorbed P (Fig. 13). For the sandy soil samples ($n=27$) a better fit between P-AL and adsorbed P is derived (fig. 15; $V^2=97.2$):

$$P-AL = -5.67 - 258.1 \frac{P_i}{(Al+Fe)_{ox}} + 125.9 \frac{P_{ox}}{(Al+Fe)_{ox}} + 12.34 P_i \quad (48)$$

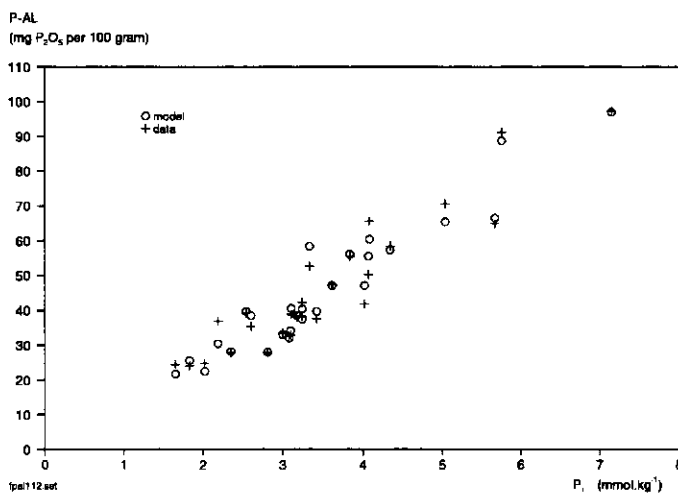


Fig. 14 Measured (+) and predicted (o) P-AL-value as a function of the amount of adsorbed P (P_i)

The P-AL-value of a soil sample can be estimated by means of equation 48. The effect of low application rates on the decrease in P-AL-value can be estimated, as follows:

The annual P application is distributed over a few P pools:

$$P_{appl} = P_{upt} + P_{fix} + P_{immob} + P_{leach} \quad (49)$$

P_{appl}	= P application	(kg ha ⁻¹)
P_{upt}	= nett P uptake by plants	(kg ha ⁻¹)
P_{fix}	= anorganic P fixation	(kg ha ⁻¹)
P_{immob}	= nett organic P immobilisation	(kg ha ⁻¹)
P_{leach}	= P leaching	(kg ha ⁻¹)

The decrease in P-AL-value is fully caused by the decrease in adsorbed P. The decrease in adsorbed P (after one year) can be calculated from:

$$\Delta Q = \frac{100 * (P_{upt} + P_{immob} + P_{fix} + P_{leach} - P_{appl})}{31 * \rho_d * LD} \quad (50)$$

ΔQ	= decrease in the amount of adsorbed P	(mmol kg ⁻¹)
ρ_d	= density of the soil	(kg.m ³)
LD	= the thickness of the soil layer considered	(m)
100/31	= a factor to convert kg ha ⁻¹ P in mmol kg ⁻¹ P	

If P_{short} is defined as:

$$P_{short} = P_{upt} + P_{immob} + P_{fix} + P_{leach} - P_{appl} \quad (51)$$

P_{short}	= P shortage	(kg ha ⁻¹)
-------------	--------------	------------------------

equation (43) will become

$$\Delta Q = \frac{100 * P_{short}}{31 * \rho_d * LD} \quad (52)$$

As a result of this decrease in the amount of adsorbed P, a new status of the amount of adsorbed P can be calculated:

$$(P_i)_{t+1} = (P_i)_t - \Delta Q \quad (53)$$

Substituting equation (53) in equation (48) the decrease in P-AL-value can be modelled.

Since, the decrease in P-AL-value is fully determined by the decrease in adsorbed P, a second method is also possible.

Using the P-AL-method all reversibly bound P is dissolved and also a part of the P which has diffundated into the soil aggregates. In formula:

$$P-AL = p (Q_o + \epsilon S_o) \quad (54)$$

- Q_o = amount of adsorbed P (mmol kg⁻¹)
 ϵ = fraction of the total amount diffundated P (S_o) which is extracted by the ammonium-lactate-acid method (-)
 S_o = total amount P which is diffundated in aggregates (mmol kg⁻¹)
 p = factor converting mmol kg⁻¹ P to mg P₂O₅ per 100 gram (mg P₂O₅ per 100 g kg mmol⁻¹)

If from a soil sample the P-AL-value and amount of adsorbed P (Q_o) is determined (by means of P_f-method), the value of $\epsilon \cdot S_o$ can be calculated from equation (54).

The development of the P-AL-value as a function of time can be predict by:

$$(P-AL)_{t+1} = \tau + p Q_{t+1} \quad (55)$$

- $\tau = p \epsilon S_o$ = a part of the amount of P which is diffundated in soil aggregates and which can be extracted by means of the ammonium-lactate-acid solution (P-AL-method) (mg P₂O₅ per 100 g)

Figure 15 shows the decrease of the P-AL-value estimated by means of both methods (Al+Fe_{ox} = 80 mmol kg⁻¹; Q_o=4.4 mmol kg⁻¹; P-AL=50 mg P₂O₅ per 100 g; LD=0.2 m; ρ_d = 1300 kg.m⁻³).

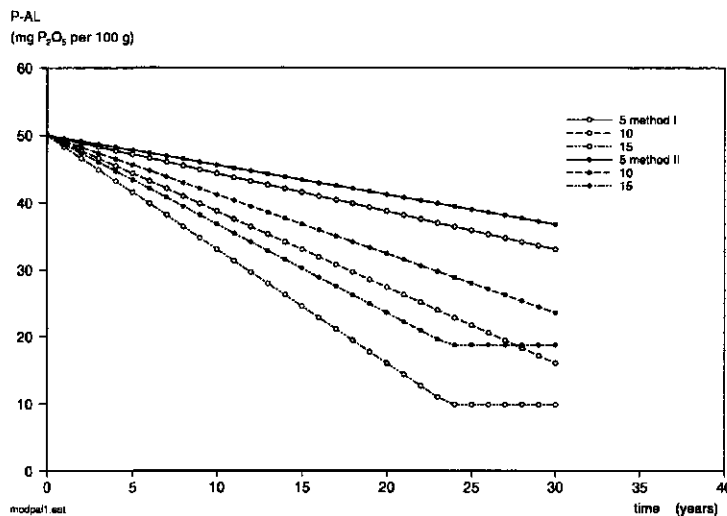


Fig. 15 The decrease of the P-AL-value at a P-shortage of 5, 10, and 15 kg ha⁻¹ a⁻¹ predicted according to method I and method II (see text)

In this examples, within 25 years all the reversibly bound P is removed in situations with relative high P shortages (15 kg ha⁻¹ a⁻¹). Under these conditions the P-AL-value will become stable (see equation 48 for method I and equation 55 for method II).

There are no field experiments available where the total balance is measured, including the changes of soil chemical P pools, organic P pools and amount of P leaching. Therefore, these two methods can not be validated. Since, laboratory experiment (fig.

13) showed that, in situation which P-shortage, the decrease in P-AL-value can be explained by the decrease of the amount of adsorbed P, method II is probably the most reliable method under these conditions.

4 The effect of P leaching on soil P fertility parameters

If the annual P application rate is equal to the sum of the amount of P uptake, nett P immobilisation and P fixation, the decrease in soil P level is fully caused by the amount of P leaching. From equation (51) follows:

$$P_{short} = P_{leach} \quad (56)$$

In the Netherlands organic P leaching from the top soil (non-calcareous sandy soils) varies between 20-40% of the total amount of P leaching (Schoumans en Kruijne, 1995). From the soil chemical properties of the soil, the amount of anorganic P leaching can be calculated. If also the amount of organic P leaching is taken into account (e.g. 30% of the total amount of P leaching) the soil fertility P parameter will drop faster, because of the increase of P shortage. In figure 16a the decrease of the Pw-value, caused by phosphorus leaching at an precipitation surplus of 300 mm, is shown for a tillage layer (0.20 m) which contains an oxalate extractable $(Al+Fe)_{ox}$ content of 50 mmol kg^{-1} . For each initial Pw-value the decrease in Pw-value is drawn by two, inclusive and exclusive organic P-leaching. The area between these two lines is filled up. In figure 16b is shown that at Pw-values of $100 \text{ mg P}_2\text{O}_5$ per liter soil high P losses will occur ($10\text{-}15 \text{ kg ha}^{-1} \text{ a}^{-1} \text{ P}$). As a result of these high losses the Pw-value will drop fast (fig. 16a). In figure 17a and 27b the same curves are drawn for a tillage layers which contains an $(Al+Fe)_{ox}$ content of 110 mmol kg^{-1} and the same initial Pw-values. Because of these higher amounts of Al and Fe, and the resulting low P concentrations in solution, the P losses are three times lower. As a result the decrease of the Pw-value is lower.

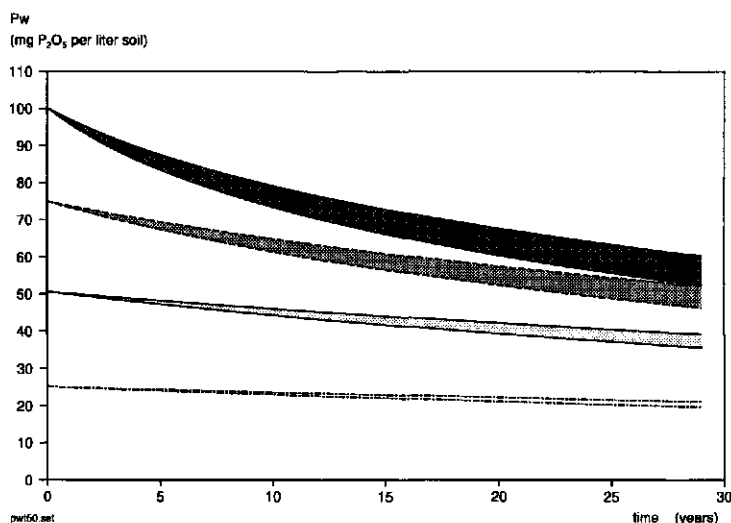


Fig. 16a The decrease of the Pw-value caused by phosphorus leaching (as a result of this Pw-value) at an $(Al+Fe)_{ox}$ content of 50 mmol kg^{-1} . Filled area: inclusive and exclusive 30% organic P-leaching

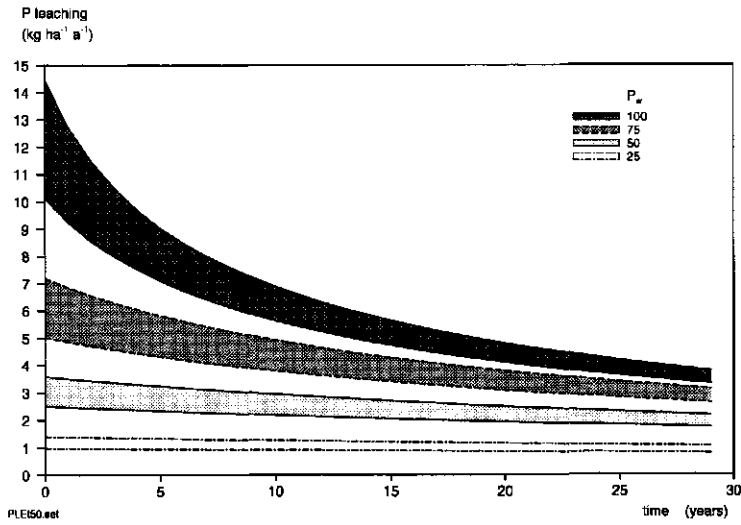


Fig. 16b The decrease of P leaching at different initial P_w -values and an $(Al+Fe)_{ox}$ content of 50 mmol kg^{-1} . Filled area: inclusive and exclusive 30% organic P-leaching

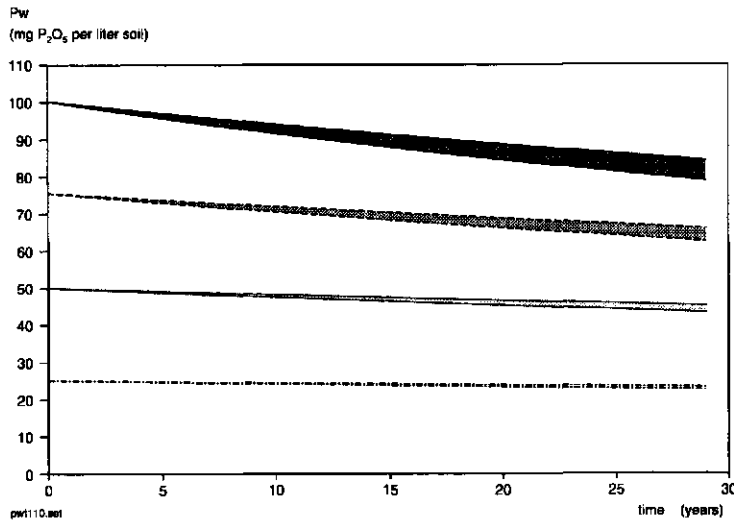


Fig. 17a The decrease of the P_w -value caused by phosphorus leaching (as a result of this P_w -value) at an $(Al+Fe)_{ox}$ content of 110 mmol kg^{-1} . Filled area: inclusive and exclusive 30% organic P-leaching

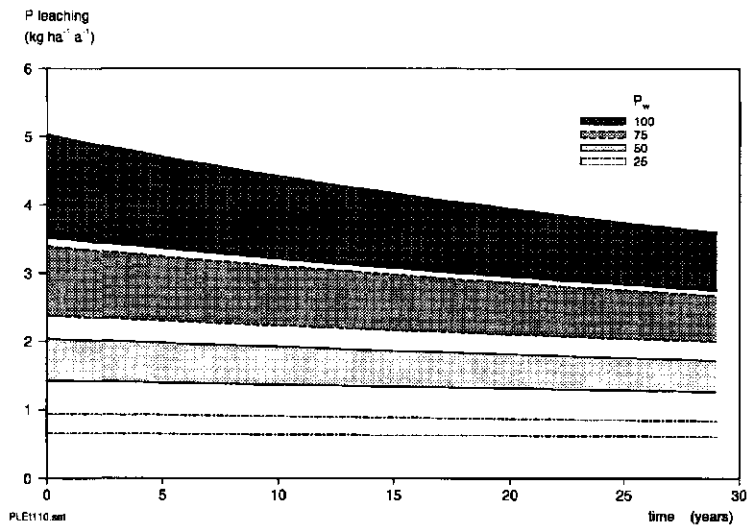


Fig. 17b The decrease of P leaching at different initial P_w-values and an (Al+Fe)_{ox} content of 110 mmol kg⁻¹. Filled area: inclusive and exclusive 30% organic P-leaching

In paragraph 3.4 relationships between Al_{ox}+Fe_{ox} content, the desorption fraction and P_w levels were presented (fig. 11). Based on these characteristics it is possible to calculate the amount of anorganic P leaching under given circumstances (figure 18). The (Al+Fe)_{ox} content is restricted to a range of 50 to 110 mmol kg⁻¹, because these values are representative for tillage layers of non-calcareous sandy soils. Leaching rates decreases at lower excess rainfall as shown in fig. 19.

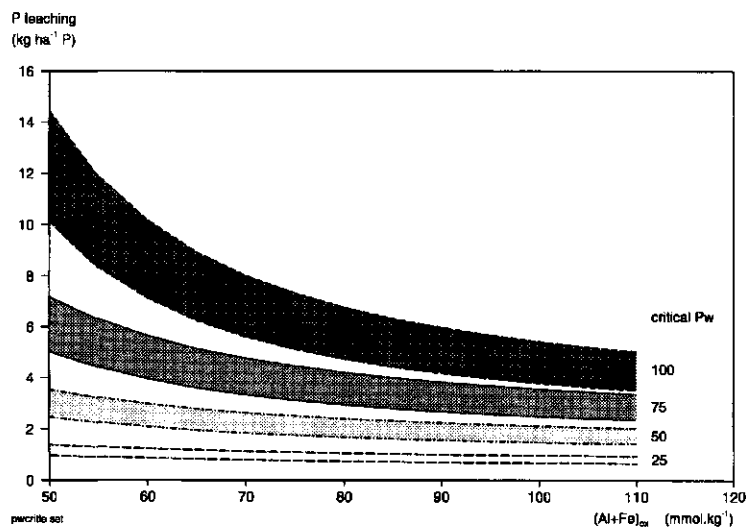


Fig. 18 The annual amount of P leaching (ortho-P and total-P) at different P_w levels as a function of the (Al+Fe)_{ox} content of the tillage layer

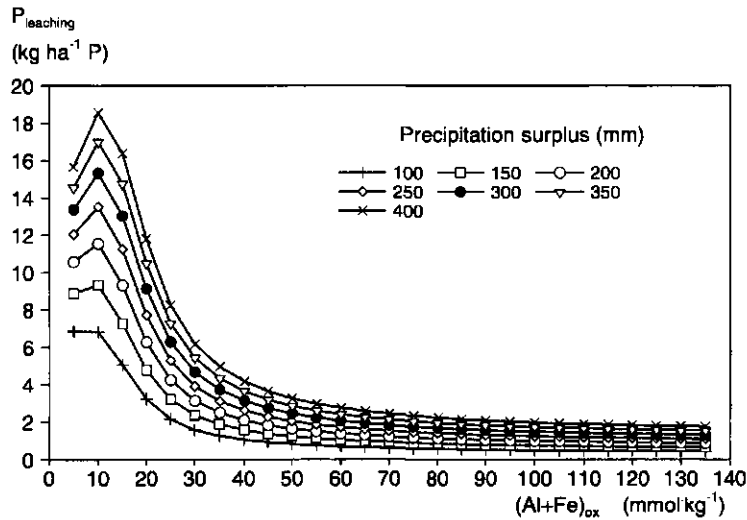


Fig. 19 The annual amount of P leaching (ortho-P) as a function of the $(Al+Fe)_{ox}$ content of the tillage layer and different levels of net precipitation surplus at a Pw value of 50 mg P_2O_5 per liter soil.

If besides P leaching also a shortage of P is caused by organic P immobilisation and/or anorganic fixation, the Pw-value will drop faster. This is shown for a situation where in addition to P leaching also a fixed annual P shortage of 15 kg P is taken into account (figure 20a). At an $(Al+Fe)_{ox}$ content of 50 mmol kg⁻¹ the Pw-value is reduced to 50% of the original value within about 10 years. At a content of 110 mmol kg⁻¹ this reduction is reached within 20 years (fig. 20b).

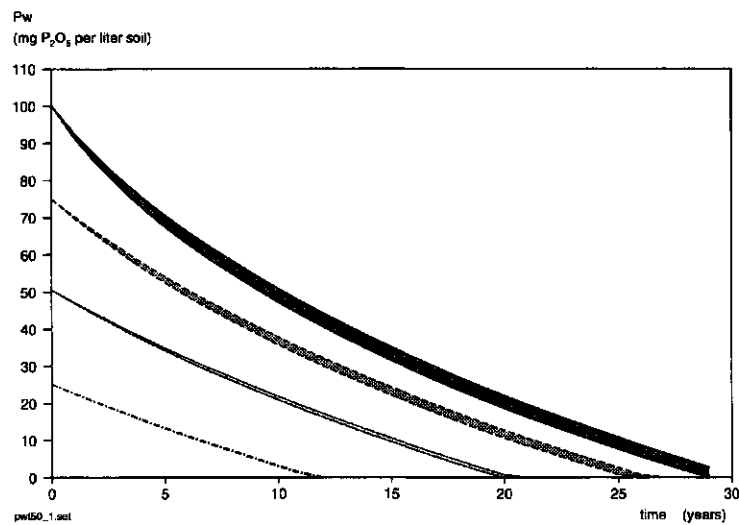


Fig. 20a The decrease of the Pw-value caused by phosphorus leaching and a fixed P-shortage of 15 kg P at an $(Al+Fe)_{ox}$ content of 50 mmol kg⁻¹. Filled area: inclusive and exclusive 30% organic P-leaching

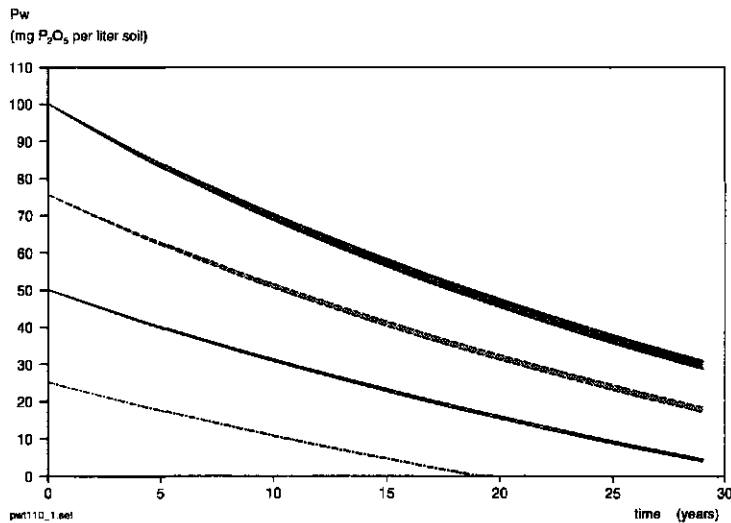


Fig. 20b The decrease of the Pw-value caused by phosphorus leaching and a fixed P-shortage of 15 kg P at an $(Al+Fe)_{ox}$ content of 110 mmol kg^{-1} . Filled area: inclusive and exclusive 30% organic P-leaching

The reduction of the P-Al-value is rather difficult to assess, because the same P-AL-value can occur under different soil chemical conditions (equation 41). In the tillage layer of non-calcareous sandy soils, the amount of adsorbed P (Q_0 which can be extracted with the iron paper method; P_i) is about 1/5 to 1/3 of the total amount oxalate extractable P. Furthermore, the $(Al+Fe)_{ox}$ content of these soils varies between 50 and 110 mmol kg^{-1} . If we assume for a certain tillage layer an $(Al+Fe)_{ox}$ content of 80 mmol kg^{-1} and a Q_0 - P_{ox} -ratio of 1/3, the Q_0 and P_{ox} value can be calculated for different P-AL-values. Based on these initial conditions the reduction of the P-AL-value can be estimated. In paragraph 3.4 it is supposed that method II ($P-AL_{t+1} = \tau + p Q_t$) is probably the best method. Since, the P-AL-value is mostly used for pasture (thin tillage layer), calculations have been carried out for both a tillage layer of 0.2 m and 0.05 m (fig. 21a and 21b). If the P shortage is limited to the upper 0.05 m of the soil, the P-Al-value will drop rather fast (fig. 20b). If all the adsorbed P has been used for plant uptake, and the amount of diffundated P is not available for plant uptake ('irreversibly bound P'), the P-AL-value will become stable ($\tau = p \in S_0$; Eq. 54). In practice, probably the P-AL-value will decrease below the value of τ , because under these circumstances (very low P concentrations and a very low Pw-value) a part of the amount of diffundated phosphate will desorb (Lookman, 1995).

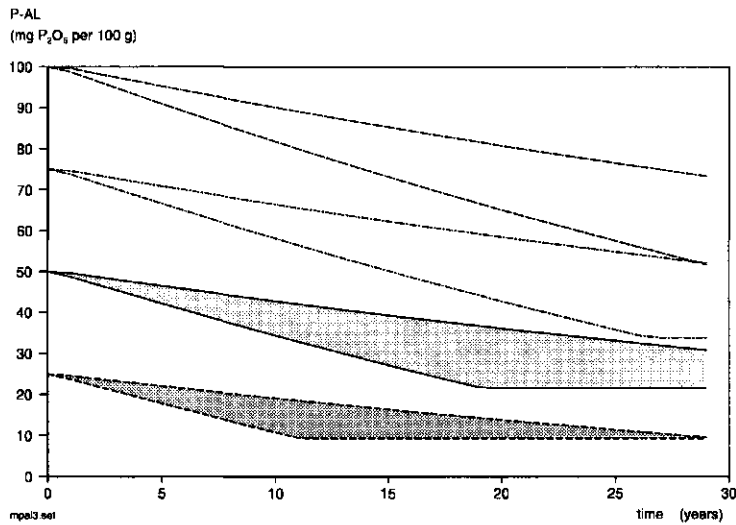


Fig. 21a The decrease of the P-AL-value caused by anorganic phosphorus leaching and a fixed P-shortage of 5 kg P ha⁻¹ a⁻¹ (filled area) for a tillage layer of 0.20 m (left) and 0.05 m (right) and an (Al+Fe)_{ox} content of 80 mmol kg⁻¹

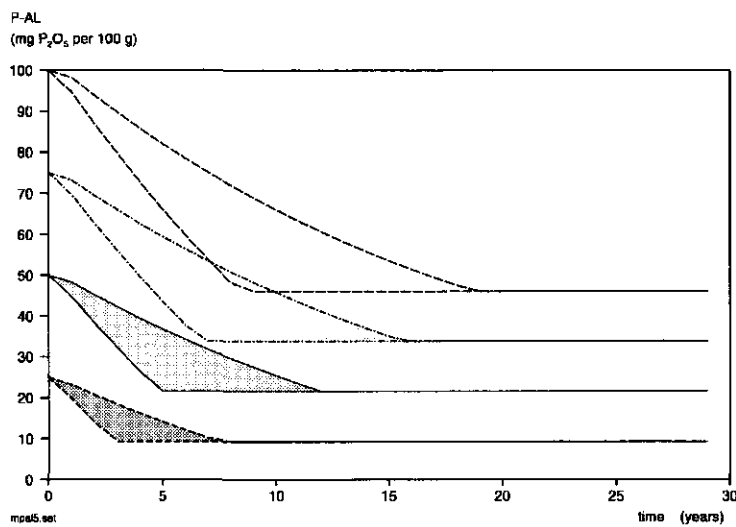


Fig. 21b The decrease of the P-AL-value caused by anorganic phosphorus leaching and a fixed P-shortage of 15 kg P ha⁻¹ a⁻¹ (filled area) for a tillage layer of 0.20 m (left) and 0.05 m (right) and an (Al+Fe)_{ox} content of 80 mmol kg⁻¹

5 Conclusions

- 1 Based on the description of P sorption and desorption kinetics, it is possible to derive a description of P availability. Therefore, deterministic models can be very helpful in analyzing the nature of the surplus of P that may be needed to maintain optimum soil P levels.
- 2 If the P availability is based on a water extraction (such as P_w), a very good prediction has been found. Since, the P_w parameter is determined at a short desorption time after dilution (1 hour), it is important that the decrease in adsorbed P, as a result of dilution, and the desorption time itself is taken into account (non-equilibrium situation).
- 3 Non-water extractions (such as P-AL) extract besides the amount of reversibly adsorbed P, also a part of the amount of phosphorus which is bound at the surface of micropores. This diffundated P is very strongly bound and will not desorb under normal agricultural conditions. Therefore, the P concentration in solution is determined by the amount of adsorbed P.
- 4 If the P availability is based on a non-water extraction, multiple regression models can be used to predict the P-AL-value. These models are probably only valid for situations where the P-AL-value has continuously increased. Laboratory experiments show that the decrease in P-AL-value can be fully explained by means of the decrease of the amount of adsorbed P. Therefore, the decrease in P-AL-value caused by P leaching or P shortage (in relation to P requirements), can be predicted on basis of the phosphate desorption kinetics of the soil. It is important that this method to predict the decrease of P availability of non-water extractions is validated in the near future.
- 5 Environmental losses of P by leaching from the tillage layer to deeper layers depend on soil P level and vary in non-P saturated soils from 1-2 kg ha⁻¹ a⁻¹ P at medium soil P levels to 3-15 kg ha⁻¹ a⁻¹ at high values.
- 6 The rate of the decrease of the P_w-value is determined by initial P_w-value, the amount of P shortage, and the sum of the amount of oxalate extractable aluminium and iron (Al+Fe)_{ox}. Furthermore, the decrease in P leaching is also determined by these parameters. For example, at a P shortage of 15 kg ha⁻¹ a⁻¹ P the initial P_w-value of a tillage layer (0.2 m) is reduced to 50% within 10 years at an (Al+Fe)_{ox} content of 50 mmol kg⁻¹ and 20 years at an (Al+Fe)_{ox} content of 110 mmol kg⁻¹.
- 7 The decrease of the P-AL-value is determined by the initial P-AL-value, the amount of P shortage, and the sum of the amount of oxalate extractable aluminium and iron (Al+Fe)_{ox}. Since the P-AL-value is frequently used for pasture with a thin tillage layer (0.05 m), the reduction of the P-AL-value is much higher compared to the reduction in a 0.2 m layer (assuming that the P shortage is fully restricted to the involved tillage layer). For example, at a P shortage of 15 kg ha⁻¹ a⁻¹ P the initial P-AL-value of a tillage layer (0.05 m) is reduced to 50% within 5-10 years at an (Al+Fe)_{ox} content of 80 mmol kg⁻¹. At a tillage layer of 0.2 m the 50% reduction time is about 10-30 years (depending on the initial P-AL-value).

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